The Nucleus, **46** (3) 2009 : 125-137

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

RECENT RESULTS FROM MILAGRO FIELD CAMPAIGN 2006 IN THE MEXICO MEGACITY

L.T. MOLINA, S. MADRONICH[1], J.S. GAFFNEY[2], H.B. SINGH[3] and *G. SOSA[4]

Molina Center for Energy and the Environment, La Jolla, CA USA

[1]National Center for Atmospheric Research, Boulder, CO. USA

[2]University of Arkansas at Little Rock, AR. USA,

[3]NASA Ames Research Center, Moffett Field, CA. USA

[4]Instituto Mexicano del Petróleo, México, D. F., México.

The air quality in large urbanized regions represents one of the major threats to the public and the ecosystems health. A number of harmful compounds emitted to the atmosphere from the various human activities increase the risk of having undesired illnesses, and possible death. Secondary air pollutants in both, air and aerosol phase, contribute to worsening this situation. on the other hand, there is an increasing recognition that air quality and climate change are strongly connected. Ozone plays an important role in this connection, apart from being by itself a greenhouse gas. This interaction is expected to evolve in response to changes in man-made emissions of gas precursors and to changes in physical climate. In this paper, a general scheme of the tropospheric ozone formation will be presented, as well as the current results from the MILAGRO field campaign took place in the Mexico Megacity in 2006.

Keywords : MILAGRO, Air pollution, Mexico city, Urban atmosphere

1. Introduction

About half of the world's population now lives in urban areas, of which 70% lives in less-developed regions [1]. Many of these urban centers are expanding rapidly, leading to the growth of cities and megacities (urban areas with over 10 million inhabitants). Population growth, increasing industrialization and motorization have resulted in a higher demand for energy and therefore, more emission of pollutants into the atmosphere. Air pollution is one of the most important environmental challenges of this century. This challenge is particularly acute in the developing world where the rapid growth of megacities is producing atmospheric pollution of unprecedented severity and extent [2, 3].

There is growing recognition that these airborne missions from major urban and industrial areas influence both air quality and climate change on scales ranging from regional upto global. Urban/industrial emissions from the developed world, and increasingly from the megacities of the developing world, change the chemical content of the downwind troposphere in a number of fundamental ways. On a larger scale, these emissions drive the production of ozone in the free troposphere, contributing significantly to global warming. Urban and industrial areas are also major sources of greenhouse gases (CO_2, CH_4, N_2O and halocarbons). Nitrogen oxide and sulfur oxide emissions are also processed to strong acids by atmospheric photochemistry on regional to continental scales, driving acid deposition to sensitive ecosystems. Direct urban/industrial emissions of carbonaceous aerosol particles are compounded by the emission of high levels of secondary aerosol precursors, including: NOx, VOCs, SO_2, and NH_3, resulting in the production of fine aerosol, affecting both air quality and cloud formation microphysics hundreds to thousands of kilometers downwind. The geographic re-distribution of pollutants, the evolution of their chemical, physical, and optical properties, and the mechanisms for their eventual removal from the atmosphere are very complex and partly understood at the present time.

MILAGRO (Megacity Initiative: Local And Global Research Observations) is the first

* Corresponding author : gsosa@imp.mx

international collaborative project to examine the behavior and the export of atmospheric pollutants generated in megacities. The measurement campaign was sponsored by the US National Science Foundation (NSF), Department of Energy (DOE) and National Aeronautic and Space Administration (NASA), and by many Mexican agencies, including the Mexican Ministry of the Environment (SEMARNAT), the Metropolitan Environmental Commission of the Valley of Mexico (CAM), Consejo Nacional de Ciencia y Technología (CONACyT) and Petróleos Mexicanos (PEMEX). It involved the participation of more than 150 institutions from Mexico, the United States and Europe and over 450 investigators and technicians from over 30 different nationalities.

1.1. The air quality in Mexico Megacity

The MCMA lies in an elevated basin 2240 m above sea level. The basin is surrounded on three sides by mountain ridges, but with a broad opening to the north and a narrower gap to the south-southwest (Fig. 1). During the twentieth century the MCMA experienced huge increases in population and urbanized area as it attracted migrants from other parts of the country and industrialization stimulated economic growth.

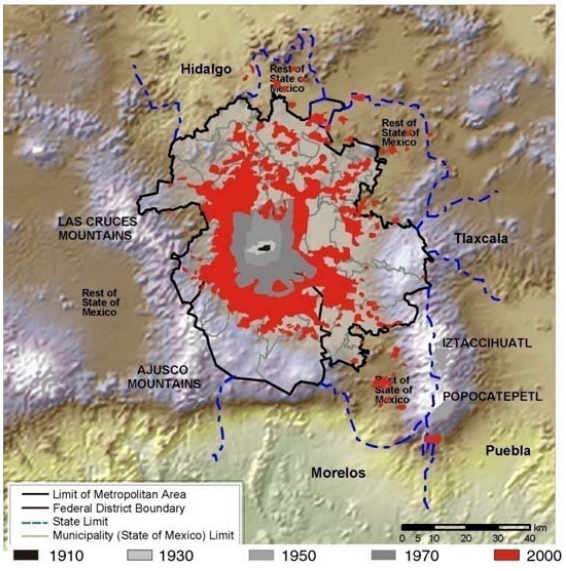

Figure 1. Topographical map of the MCMA showing urban expansion [4].

The population grew from fewer than 3 million in 1950 to over 18 million in 2000; the urbanized area now covers about 1,500 km^2 —about 10 times as much land as it occupied just 50 years ago. The metropolitan area's nearly 20 million inhabitants, over 40,000 industries and 4 million vehicles consume more than 40 million liters of fuel per day and produce thousands of tons of pollutants. The high altitude and mild climate facilitates ozone production all year and contributes to the formation of secondary particulate matter. Air pollution is generally worse in the winter, when rain is less common and thermal inversions are more frequent [4]. During the past decade, the Mexican government has made tremendous progress in improving air quality. Substantial reductions in the concentrations of some criteria pollutants (such as lead, carbon monoxide and sulfur dioxide) were achieved by developing and implementing comprehensive air quality management programs and improving air quality monitoring and evaluation programs [5, 6]. Fig. 2 shows the air quality trends. Despite these important gains, the MCMA residents remain exposed to unhealthy concentrations of air-borne pollutants, especially particulate matter (PM) and ozone, the two most important pollutants from the standpoint of public health [7]. A MCMA-2003 measurement campaign was carried out during April 2003 to cover the height of the annual photochemical season just prior to the onset of the rainy season. It involved a supersite located at the National Center for Environmental Research and Training (CENICA), a component of the National Institute of Ecology (INE) of the Ministry of the Environment, with state-of-the-art instrumentation contributed by many US and European teams. A mobile laboratory from Aerodyne Research Inc. (ARI) was deployed for measurements at various locations in the MCMA. The MCMA-2003 Campaign generated a very extensive data set and provided important scientific information that was fundamental in the planning of the larger MILAGRO Campaign. An overview article on the MCMA-2003 has been published [8].

2. Milgaro Field Campaign 2006

The MILAGRO Campaign is a large, international, multiagency, collaborative project to evaluate the regional impacts of the Mexico City air pollution plume as a means of understanding urban impacts on the global climate. Specific goals of the campaign included quantifying the spatial and temporal extent of the urban plume, analyzing pollutant chemical and physical transformation in

the plume, quantifying the regional impacts of the plume and examining the interaction of the urban plume with surrounding sources. The initial phase of MILAGRO was to conduct measurement of pollutants, which took place during March 2006.

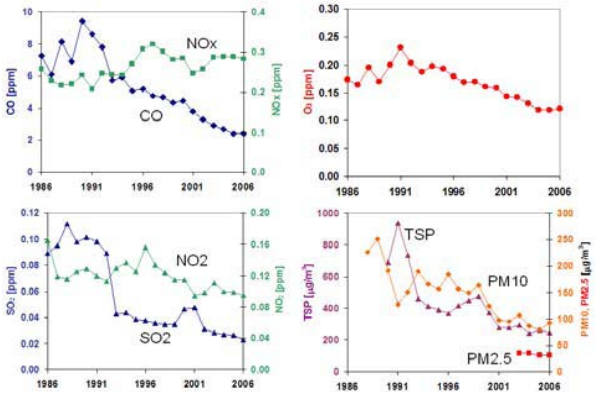

Figure 2. Air quality trends of the MCMA (Mexico City, Federal District Government 2006; www.sma. df.gob.mx/ simat).

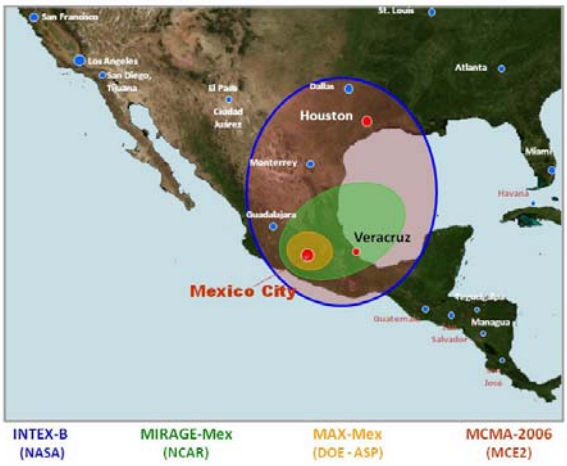

Figure 3. Geographical coverage of the MILAGRO Campaign.

The measurements included a wide range of instruments at ground sites, on aircraft, and satellites. Three supersites, spaced about 30 km apart to examine the pollutant plume evolution, were set up at the Instituto Mexicano del Petróleo (IMP, "T0"), Universidad Tecnológica de Tecamac in the State of Mexico ("T1") and Rancho La Bisnaga in the State of Hidalgo ("T2"). The designations "T0", "T1", and "T2" refer to transport of the urban plume to different points in space and time. Seven instrumented research aircraft participated in MILAGRO: five were based in Veracruz, Mexico, one in Puebla, Mexico and one in Houston, Texas. These airborne measurements provided information about the atmosphere over a large region, and at various altitudes. Satellitebased instruments peered down into the atmosphere, providing even larger geographical coverage. Fig. 3 shows the geographic coverage and Fig. 4 shows the ground-based measurement sites.

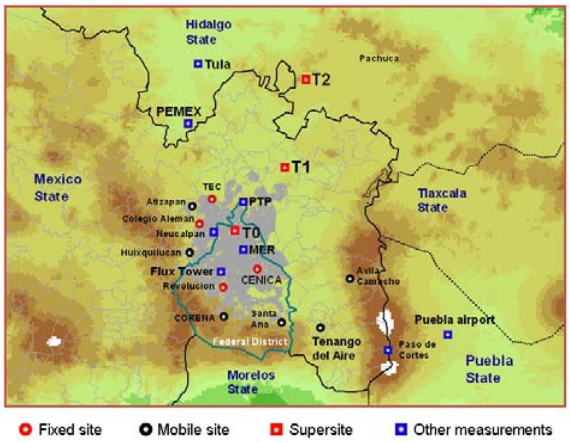

Figure 4. Ground-based measurement sites of the MILAGRO Campaign.

The MILAGRO campaign was organized under four coordinated components:

MCMA-2006 (Mexico City Metropolitan Area – 2006 Experiment) examined emissions and boundary layer concentrations within the Mexico City Basin, their transport and transformation in the atmosphere, and the effects on human health. MCMA-2006 was led by the Molina Center for Energy and the Environment (MCE2) with projects sponsored by NSF, DOE, and several Mexican research agencies, including CAM, INE, CONACyT and PEMEX, as well as European agencies. The overall purpose of the MCMA-2006 is to strengthen the scientific base for the design and evaluation of policies to improve the air quality in the MCMA by gathering scientific information that helps to elucidate the processes by which pollutants are generated in the MCMA; how pollutants are dispersed, transported and transformed in the atmosphere; the exposure patterns of the population to these pollutants; and the effects on human health. The required data on aerosols, VOCs and other gases, meteorology, and solar radiation was obtained through measurements at the T0 supersite, a flux tower located at the city center, and the Tula refinery site and industrial zone in Naucalpan, in combination

with measurements from a highly capable mobile laboratory, a microlight research aircraft and several fixed mobile units deployed throughout the MCMA at representative urban and boundary sites. In addition, two health studies were carried out during the Campaign.

MIRAGE-Mex (Megacity Impacts on Regional and Global Environments - Mexico) examined the chemical/physical transformations of gaseous and particulate pollutants exported from Mexico City, as a case study of megacities' effects on regional and global atmospheric composition and climate. MIRAGE-Mex was led by the National Center for Atmospheric Research (NCAR) in collaboration with researchers from academia under NSF sponsorship. Specific objectives were to: (1) Quantify the spatial extent and temporal persistence of the polluted outflow plume; (2) identify and quantify the chemical and physical transformations of the gases and aerosols in the plume, especially the processes that lead to the removal of these pollutants from the atmosphere; (3) quantify the effects of the plume on regional oxidants and radiation budgets, and ultimately on climate; and (4) examine the interactions of the urban plume with background air, as well as pollutants from other sources including regional anthropogenic pollutants, biomass fires, and vegetative emissions. The NCAR/NSF C-130 aircraft carried a payload of state-of-the-art scientific instruments and sampled air at different distances from Mexico City to measure how gases and particles "age" during transport, specifically tracking those chemical, physical, and optical properties that have the potential to affect air quality, weather, and climate on large geographic scales. An additional aircraft (Twin Otter) conducted studies of fires and their effect on the local and regional composition of the atmosphere. Other MIRAGE-Mex researchers were located at the T1 supersite, to examine the chemistry and physics of surface air as it first exits Mexico City.

MAX-Mex **(**Megacity Aerosol Experiment: Mexico City) focused on examining how the Mexico megacity aerosol plume would evolve during transport, and how the chemical and physical nature of the aerosol effected scattering and absorption by the aerosol. MAX-Mex was conducted by the Atmospheric Science Program of the DOE Climate Change Research Division in collaboration with the scientists supported by NSF, NASA, and Mexican agencies. Measurements were conducted using an airborne LIDAR operated by NASA scientists with support from DOE, the DOE Gulfstream-1 (G-1) airborne platform that obtained gas and aerosol measurements, and three surface supersites to examine the aerosol plume evolution. The T0 and T1 sites were instrumented heavily with aerosol instrumentation for characterization of chemical and physical properties including the scattering and absorption of aerosols, particularly in the submicron fractions that are anticipated to have the longest lifetimes and have the most impact on regional and potentially global climate forcing.

INTEX-B (Intercontinental Chemical Transport Experiment- B) was an integrated field campaign designed to understand the transport and transformation of gases and aerosols on transcontinental/intercontinental scales and to assess their impact on air quality and climate. Central to achieving this goal was the need to relate space-based observations with those from airborne and surface platforms. Specific INTEX-B/MILAGRO objectives were to: (1) investigate the extent and persistence of the outflow of pollution from Mexico; (2) understand transport and evolution of Asian pollution and implications for air quality and climate across western North America; (3) map anthropogenic and biogenic emissions and relate atmospheric composition to sources and sinks; (4) characterize the effects of aerosols on solar radiation; and (5) validate space-borne observations of tropospheric composition.

The INTEX-B /MILAGRO campaign was performed in two parts in the spring of 2006. The first part focused on pollution over Mexico City (March 1-21) and the second part on transported pollution from Asia (April 17-May 15). In the first part, the DC-8 operated from Houston, TX with sorties over Mexico and the Gulf of Mexico while the J-31 and NSF/NCAR C-130 operated from Veracruz, Mexico. In the second part, the DC-8 was based in Honolulu, Hawaii (April 17-30) and Anchorage, Alaska (May1-15) with the NSF/NCAR C-130 operating from Seattle, Washington (April 17-May 15) in a coordinated fashion. The overall experiment was supported by forecasts from meteorological and chemical models, satellite observations, surface networks, and ozonesonde data. Fig. 5 shows the DC-8 tracks during INTEX-B/MILAGRO and locations of key airborne

platforms. Through these in-situ and remote, a large body of atmospheric composition data has been acquired over Mexico and the Pacific. To assist in the analysis of these data, global and regional models have been run that provide simulations along the aircraft flight tracks.

3. Preliminary Results from Milagro Campaign

The MILAGRO Campaign generated a very comprehensive data set and many interesting results have emerged over the past year. The observations from MCMA-2003 Campaign were mostly confirmed during MILAGRO; additionally MILAGRO provided more detailed gas and aerosol chemistry, aerosol microphysics and optics, radiation and wider regional-scale coverage. In the following sections, we present some preliminary results.

3.1. Meteorology (urban/regional)

The MILAGRO Campaign provided extensive meteorological measurements of one of the largest urban areas in the world. The meteorological situation during

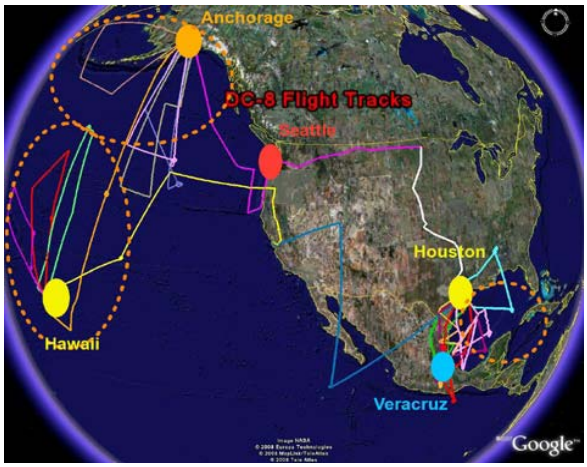

Figure 5. INTEX-B DC-8 flight tracks and DC-8 Bases in Houston, TX (3/1-21/2006), Honolulu, Hawaii (4/17-30/2006), and Anchorage, Alaska (5/1-15/2006). Also shown are operational sites for the: DC-8 (yellow ovals); C-130 (red oval); and C-130, J-31, B-200, G-1 (blue oval).

MILAGRO has been reviewed by [9]. The MILAGRO campaign was characterized by six types of meteorological episodes, representing different wind transport regimes [10], which were used in data analysis. This is in contrast to three episode types during MCMA-2003 [11]. The month of March is near the end of the dry season, and 2006 was not atypical compared to previous field campaigns. The early part of the month was mostly clear and dry over the plateau, but increasingly humid and convective toward the end of the month. On most days the large scale flows were relatively weak and predominantly toward the Gulf of Mexico, but also with some regional scale recirculation. In agreement with previous studies, planetary boundary layer (PBL) heights (measured by radiosondes, profilers, and surface- and aircraft-based lidars), grew rapidly during late morning and exceeded 4 km agl on some days [12], with frequent complex layering [13]. Night-time PBL depths were variable and tended to be higher than model predictions, likely due to urban perturbations. The orography surrounding MCMA leads to complex surface winds, but the basin is ventilated on a daily basis, with little day-to-day accumulation of pollutants [14, 10]. The rapid PBL growth and its collapse in the late afternoon lead to the entrainment of polluted air into the free tropospheric synoptic flow. This was particularly clear on March 18th and 19th, when stronger southwesterly winds carried pollutants from Mexico City towards the coastal Mexico-Texas border (Fig. 6). This allowed quasi-Lagrangian sampling of the air, on March 18th near MCMA by the G-1 aircraft, and on March 19th downwind by the C-130 aircraft. Altitude-controlled balloons confirmed these trajectories [15].

3.2. Emissions measurements

Characterizing and quantifying the emissions of both gaseous pollutants and primary PM is a difficult task in any major urban area, but it presents a particularly daunting task in a rapidly developing megacity like the MCMA. Fig. 7 presents the 2004 MCMA emissions inventory for PM10, PM 2.5, VOC and NO_x.

Mobile emission sources represent a significant fraction of the total anthropogenic emissions burden. Observations from the 2003 study show that MCMA motor vehicles produce abundant amounts of primary PM, elemental carbon, particle-bound polycyclic aromatic hydrocarbons (PAHs), CO and a wide range of air toxics, including formaldehyde, acetaldehyde, benzene, toluene, and xylenes [8].

Several innovative techniques have been developed to evaluate the official emission inventories used in air quality models. Two innovative techniques employed during MCMA-2003 and again during MILAGRO/ MCMA-2006 are discussed here.

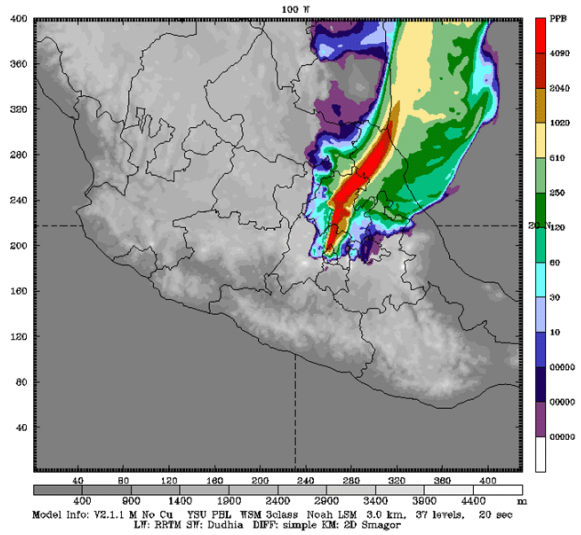

Figure 6. Distribution of Mexico City CO-like transport tracer emitted on 18 March 2006, shown on 19 March 2006 18:00 local time, as calculated using NCAR's WRF model. (*Courtesy: W. Skamarock*).

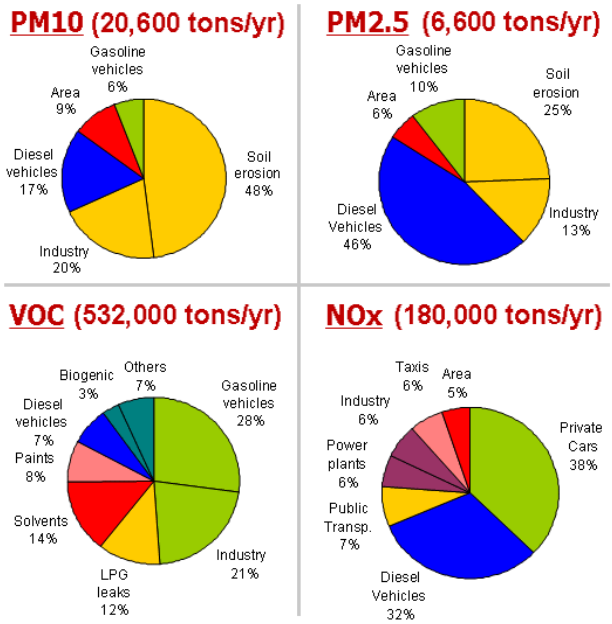

Figure 7. Emission Sources in Mexico City for the year 2004 [16].

The feasibility of using eddy covariance techniques coupled with fast-response sensors to measure fluxes of volatile organic compounds (VOCs) and CO_2 from a residential district was demonstrated for the first time during the MCMA-2003 Campaign [17, 18]. Those flux measurements showed good agreement with the local emissions inventory used for air quality modeling. A second flux system in a different district located near the center of Mexico City was set up during the MILAGRO campaign (see Fig. 8).

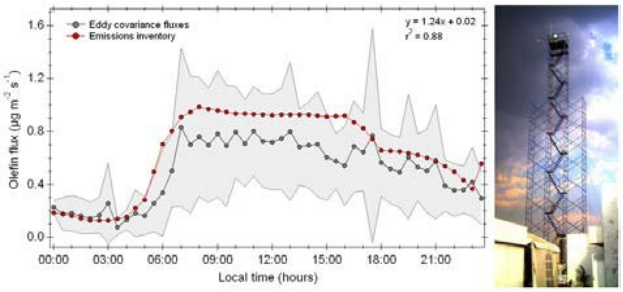

Figure 8. Measured olefin fluxes *vs.* estimated emissions as given in the local emission inventory [19].

Although these measurements did not address the full suite of VOC emissions and corresponded to only one location of the city, they again validated the emissions provided by the local authority [19]. The fluxes of speciated aerosols were also measured using an Aerodyne Aerosol Mass Spectrometer [20]. During the 2002/2003 MCMA and the 2006 MILAGRO field campaigns in Mexico City, the ARI Mobile Laboratory measured on-road vehicle fleet emission indices in fleet-average mode for various vehicle classes and driving speeds [21]. Measurements of NOX, CO, key VOC species and particle mass (PM1) and composition from surrounding vehicles were obtained. Species emission ratios to CO_2 are converted to grams of pollutant to liter of burned fuel for estimating total emissions. Fig. 9 presents the measurements of emission ratios from the 2006 MILAGRO Campaign and comparisons with the MCMA emissions inventory estimates and past measurements of mobile emissions. In addition, on-road emission ratios measurements ($HCHO/CO_2$) were obtained during the transit of the ARI mobile lab between the stationary monitoring sites, providing information on the spatial distribution of mobile emissions within the city [22]. During the 2006 campaign, high aerosol concentrations were observed both at ground sites

and from all aircraft. These aerosol particles were composed in large part of organics, but black carbon, crustal matter, sulfate and nitrate were also significant contributors. Biomass burning–agricultural, forest, and trash fires – all contribute to the urban and regional pollution of this area [23, 24, 25, 26].

3.3. Urban and regional photochemistry

3.3.1. Urban ozone production

Photochemical production of ozone is high in Mexico City due to high co-emissions of NOx and VOCs, which provide elevated radical sources – the driving forcing for urban photochemical reactivity. Radical (OH, HO_2, and RO2) measurements were made at the T0 and T1 surface sites, and onboard the C-130 aircraft. Surface radical production is particularly strong during the morning hours, and OH measurements are in fair agreement with model predictions, while peroxy radicals consistently exceeded model expectations at high NOx [27, 28, 29]. Zheng et al. observed that HNO_3, primarily produced by the reaction of OH with NO_2, was regulated by gas/particle partitioning [30].

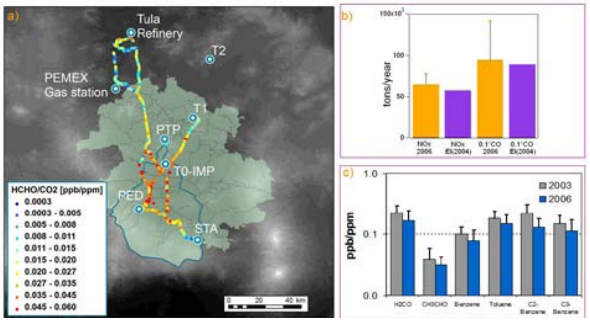

Figure 9. Shown are data used to characterize mobile emissions in Mexico City using data from the MCMA-2003 and MCMA-2006 campaigns. a) Observed highly heterogeneous spatial distributions of emissions, b) on-road measurements (orange) vs those in the local emissions inventory (purple); c) measured reduction of VOC emission ratios in the MCMA [22].

Both measurements and chemical transport model simulations suggest that O3 production in the source region is VOC-limited during photochemically active periods. For example, groundbased measurements from MCMA-2003 showed that the primary sink of HO_x is the OH + NO_2 reaction [31]; aircraft observations during MILAGRO-2006 found abundant NOx oxidation products but relatively low H_2O_2 [32], the indicator species for O_3 production sensitivity. These measurements revealed higher VOC/NO_2 reactivity ratios in the MCMA than in other cities. Chemical transport model simulations strongly indicated that O_3 formation is VOC limited during the MCMA-2003 campaign [33, 34], and the O_3 formation sensitivity is weakly dependent on meteorological conditions (Fig. 10) [35]. The O3 production rate is dominated by the radical production rate, which is attributed not only to the photolysis of O_3 and formaldehyde, but also the O_3-alkene chemical processing and heterogeneous sources of HONO [36, 37]. This sensitivity has important implications for ozone reducing policy.

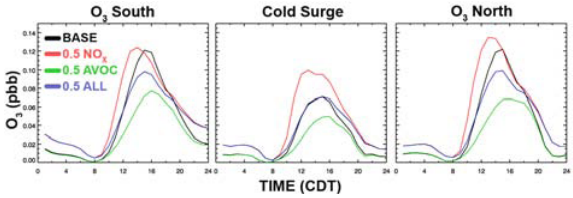

Figure 10. The response of near-surface O_3 concentrations to different emission reduction scenarios in the MCMA source region under different meteorological conditions identified during the MCMA-2003 Campaign, as given by a chemical transport model: 0.5 NOx denotes a 50% reduction in NO_x; 0.5 VOC denotes a 50% reduction in VOC; 0.5 ALL denotes 50% reductions in both NO_x and VOC emissions [35].

3.3.2. Regional chemistry

The regional impacts of the MCMA emissions are easily discernible, especially to the south-east, south, and west where MCMA provides the dominant influence. Pollution over the Gulf of Mexico is persistent and apparently due to diverse sources from the south-eastern U.S., Mexico, and Central America. In addition to urban pollutants, there is clear evidence for widespread gases and PM from biomass burning. Although the contribution of the MCMA pollutants to the Gulf region is not always easily identified, several encounters of the MCMA plume were forecast and were measured by the C-130 instruments. This was particularly clear during the March 18-19th quasi-Lagrangian episode, where an enhanced O_3:CO ratio (Fig. 11) was observed ~1000 km downwind, indicating ongoing O_3 production during the outflow.

Aircraft observations show that aldehydes are the most reactive VOCs both in the urban PBL and in the regional outflow [38]. This is also predicted

by the WRFChem model (Tie et al., in prep.). Peroxyacetyl nitrates (PANs) are the main reactive nitrogen species in the outflow [39], sustaining small levels of NO_x that allow for ongoing regional O_3 production.

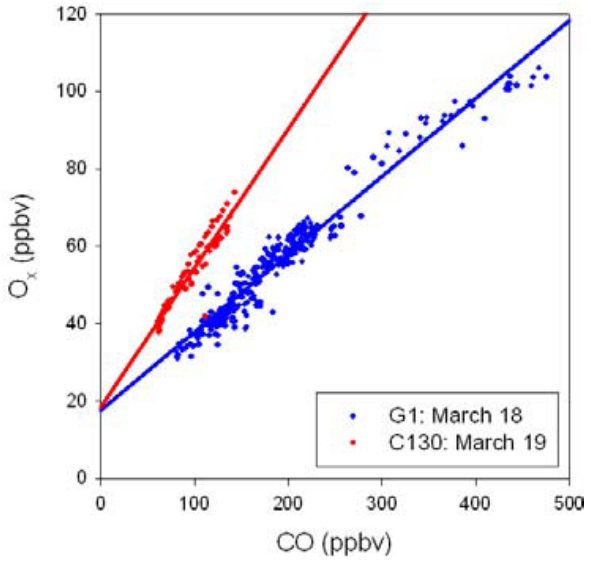

Figure 11. Evolution of O_x (= O_3 + NO_2) vs. CO correlations in the Mexico City plume. The G1 aircraft sample the air near Mexico City on 18 March (blue), while the C130 aircraft intercepted the plume about 1000 km downwind on 19 March (red) [40].

This large role of PANs is in contrast to some other megacities (Fig. 12). Modeling activities are underway to understand to what extent this is a result of the high initial VOC-NO_x mixture in the MCMA, lower temperatures at the altitude of the outflow, and/or due to contributions from regional aldehydes. On the other hand, HNO_3 was a relatively small fraction (5-20%) of the NOy in aged air, with some evidence for its loss on dust particles (see Fig. 13, [41]). A large amount of data on ozone and its precursors (VOC, OVOC, NO_x, NO_y), free radicals (OH/HO2), greenhouse gases (CO_2, CH_4, N_2O), aerosols, and a variety of tracers of urban pollution (CO, halocarbons) and biomass burning (HCN, CH_3Cl) was collected from the NASA DC-8 aircraft over wide geographic scales.

These data are currently being analyzed and interpreted using a variety of atmospheric models that are themselves being validated against observations [42]. Several manuscripts are being prepared on this topic for the MILAGRO/INTEX-B Special Issue in Atmospheric Chemistry and Physics (ACP).

3.4. Chemical evolution of aerosols

Mexico City's fine PM is usually dominated by organic species [43]. Further, fine PM was observed during MCMA-2003 to grow very rapidly during sunlight hours – far faster than current atmospheric models or laboratory simulation experiments with the expected precursor gases can explain [44]. Data collected from a mountain location in the MCMA's northeast corner during MILAGRO-2006 were used to differentiate oxygen-rich secondary organic aerosol (SOA) formed by atmospheric photochemistry from more hydrocarbonlike primary organic aerosol that is associated with MCMA vehicle PM (soot) emissions.

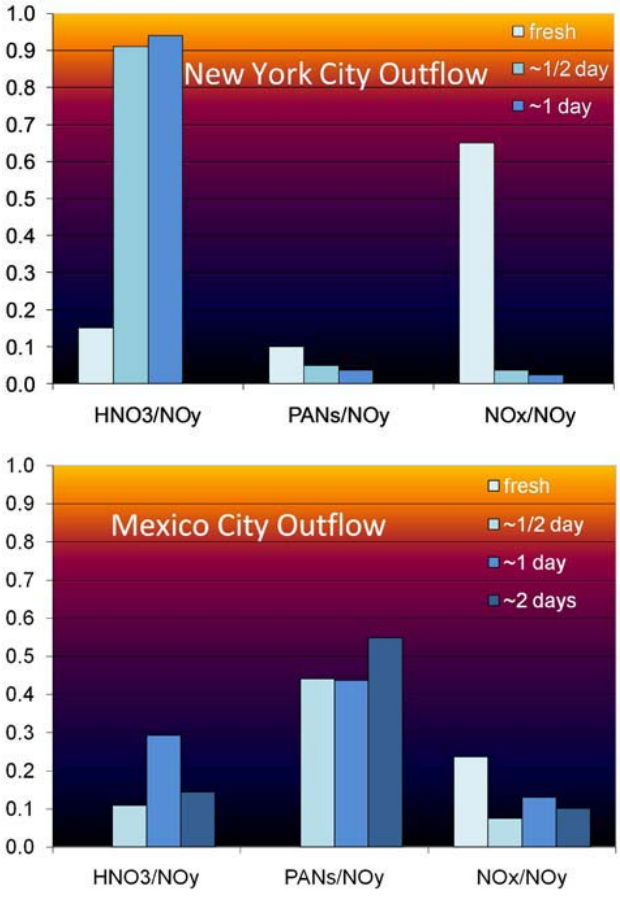

Figure 12. Reactive nitrogen in the outflow of Mexico City (bottom panel) and New York City (top panel). Downwind of Mexico City, the large fraction of PANs sustains NO_x for ongoing production of O_3 [39].

These data demonstrate a correlation between secondary organic aerosol and odd-oxygen (O_3 + NO_2), as shown in Fig. 14. The observed correlation between O_x and SOA may be used to

estimate SOA pollution levels for a range of weather conditions and emission scenarios [45].

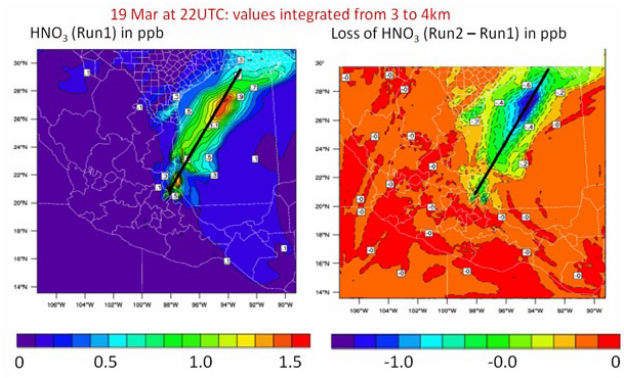

Figure 13. WRF-Chem simulation of nitric acid (HNO_3) in the Mexico City plume, without and with heterogeneous loss on dust encountered downwind. Left panel (Run 1) shows HNO_3 without loss on dust; right panel: about 2/3 of the plume's HNO_3 can be removed by this process [41].

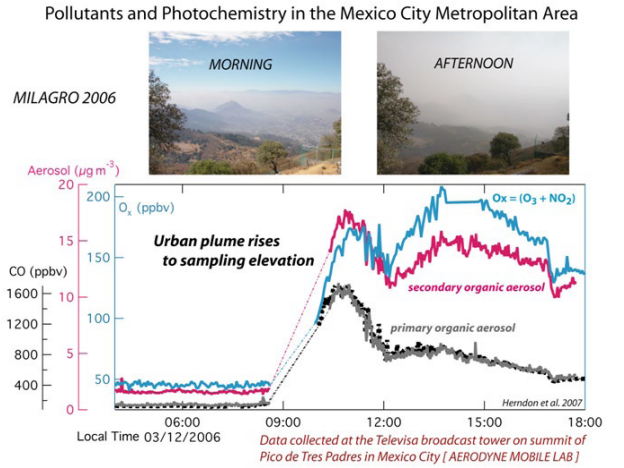

Figure 14. Photochemistry and SOA Formation in the MCMA [45].

Carbon-14 and stable carbon-13 measurements also have indicated that 45-78 % of the total carbonaceous aerosol is coming from recent carbon sources, i.e., biomass and agricultural burning activities (including trash incineration) in the MCMA. Larger amounts of biomass burning aerosols were noted at the T1 site than the T0 site, consistent with the megacity having a significant fossil fuel input, but both sites were heavily impacted by recent carbon that could be derived from local and regional burning and transport of carbonaceous aerosols.

A new method for quantifying the organic aerosol oxygen-to-carbon atomic ratio (O/C) has been recently developed using the High-Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) [46]. This method was applied for the first time to aircraft data using the results from the AMS flown in C-130 during MILAGRO-2006. Two highlights of the results are shown in Fig. 15. The left plot shows a map of the flight tracks for several C-130 flights, the organic colored by O/C ratio. There is a clear increase in O/C ratio as one moves away from the city, with maximum values around 0.9. Even above Mexico City the O/C ratio is already ~0.4 or higher, representing a highly oxygenated aerosol. This is evident in flights through the city occurring in the early to late afternoon when photochemical SOA formation has already been active for hours [44, 47]. The plot in the right side of Fig. 15 is a scatter plot of O/C vs. photochemical age calculated from NOx/NOy. Fig. 16 shows aerosol concentrations measured from the G-1 in the Mexico City urban plume as a function of photochemical age, defined by the ratio of NOx to NOy [47]. Ambient concentrations decrease with age due to plume dilution. After accounting for dilution by using CO as a conservative tracer of urban emissions, the total non-refractory aerosol and its organic component are seen to increase by factors of 5 and 7 due to secondary aerosol formation over the course of ~ 1 day. As in a previous study [44] only ~ 10% of the SOA can be accounted for by aromatic precursors.

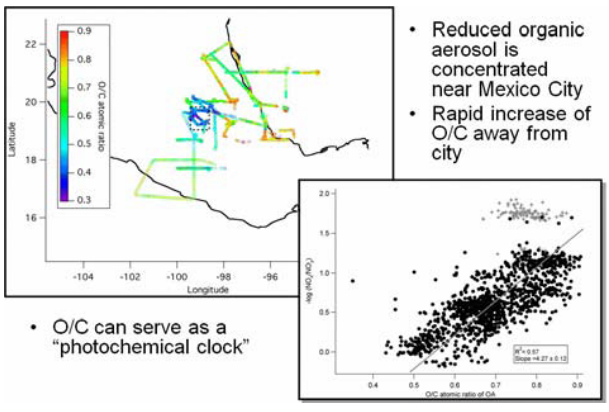

Figure 15. Organic aerosol is rapidly oxygenated in air masses originating in the MCMA [48].

Results from both ground-based and airborne measurements confirm that the megacity plumes are significant sources of both primary and secondary aerosols at the regional scale, and

black carbon and SOA are contributing to single scattering albedos in the MCMA and downwind that are substantially smaller than in other areas (such as the eastern United States). The regional burden of organic aerosol (when adjusted for dilution using CO correlations) and its O/C content ratio continue to grow with increasing air mass age for several days, and is far in excess of predictions by current models [47, 48]. Sulfate aerosol also increases relative to nitrate in older polluted air, indicating HNO_3 particle to gas partitioning.

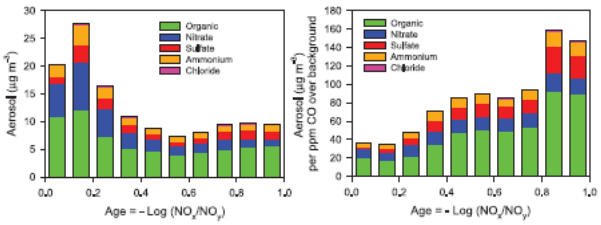

Figure 16. Secondary aerosol production in Mexico City urban plume measured from the G-1 as a function of photochemical age using – Log (NOx/NOy) as clock. Dilution is accounted for by normalizing aerosol concentration to CO above background. Left panel: Concentrations; right panel: Normalized concentrations [47].

3.5. SO_2 emissions from the Tula Industrial complex

The Tula industrial complex is located in the Valley of Mezquital, an important industrial and agricultural region located 60 km northeast of Mexico City. This region embraces several industries, such as crude oil refinery, power plant, cement-producing companies, and open pit mines for the extraction of construction materials, among other things.

As a part of the MILAGRO Campaign, an environmental monitoring took place on the physical and chemical characterization of the emission, transformation and dispersion processes of atmospheric pollutants in the Tula industrial corridor. Meteorological and dispersion models were used in conjunction with field data to simulate pollutant exchange processes between the Mezquital and Mexico Valleys. The models used were RAMS and HYPACT [49].

A regional meteorological model RAMS (Regional Atmospheric Modeling System), and the dispersion model HYPACT (HYbrid Particle And Concentration Transport) were used to better understand the SO_2 plume transport from Tula region. A three-day SO_2 dispersion simulation was conducted for three meteorological scenarios with different synoptic wind directions at 500 hPa, from: A) the Southeast, B) the West, and C) the Northeast. The first case displayed a 45.2% presence during the study period, the second 35.4% and the third 13%. The time periods selected were: 26, 27 and 28 of March for case B; 30, 31 of March and 1 April for case A, and 4, 5, and 6 of April for case C. Three-day simulation periods were selected to consider SO_2 recirculation from outside, i.e., the SO_2 transported outside the evaluation's domain, which eventually is transported back due to the change in meteorological conditions.

The dispersion of SO_2 plume is influenced by the local and regional winds. Fig 17 illustrates SO_2 dispersion from March 30 to April 1, 2006. On the first day (8 h), local winds influence the transport of

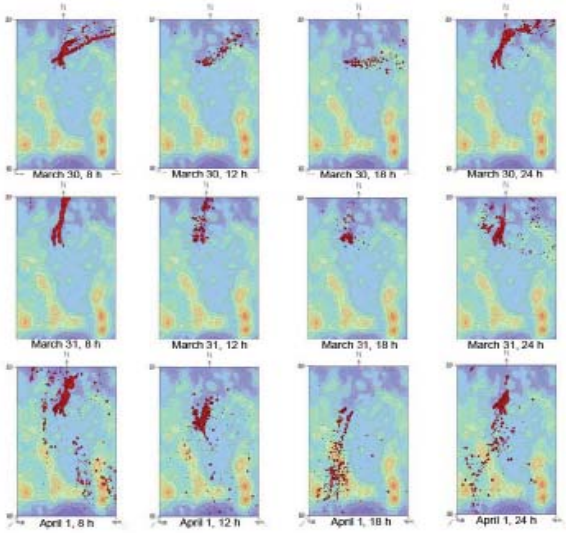

Figure 17. Ground-level sulfur dioxide isosurfaces simulated with RAMS-HYPACT, March 30 - April 1, 2006.

the pollutant plume causing it to head in a N, NNE direction; at noon (12 h), the surface wind comes from the West causing the plume to disperse toward the East, this effect is more pronounced at 18 h. By 24 h, the regional wind is generalized from the Southeast, transporting the emissions toward the NNE. On the second day the wind conditions from the Southwest persist until 8 h in the morning, displaying a very compact plume heading North of the simulation's domain. However, by 12 h, the wind shifts and blows in the

opposite direction, recirculating the morning emissions back to the Tula region. This change is not strong enough because at 24 h the regional wind has assumed again its South component. On the third day, the local wind conditions become significantly modified and from 9am the North wind component intensifies, remaining like that the whole day. This not only causes the emissions from prior days to return to the emissions source point, but also impacts the MCMA considerably, especially before midday. By 18 h, the NNE wind intensifies dispersing the SO_2 plume in a Southwest direction, without passing through the MCMA. In summary, the transport of the pollutant plume was not only influenced by synoptic conditions, but also by local winds. The variability in the local winds can cause the plume to disperse toward different directions, and may result in the recirculation when the wind shifts dramatically, which may affect indirectly the air quality in the Mexico City urban area even if the plume does not transect this area.

4. Conclusions

The observation phase of MILAGRO/INTEX-B has provided an extremely rich data set that will likely take years to analyze and evaluate. Preliminary results were presented at MILAGRO science team meetings and international conferences. Five special sessions were convened at the American Geophysical Union 2007 Fall Meeting in San Francisco, CA. Major findings are being published in a special issue on MILAGRO/INTEX-B in Atmospheric Chemistry and Physics as well as in other peer-reviewed journals.

As described above, many groups have performed comprehensive analyses, in some cases including detailed modeling, of the numerous experimental data sets obtained. Many interesting aspects of atmospheric chemistry in and near the MCMA are emerging and have already added significantly to our understanding of the chemical and physical properties of the city's reactive atmosphere and the regional impacts. Data sets will also be made available to the entire atmospheric community for further modeling and evaluation.

We anticipate new results from MILAGRO/INTEXB will continue to contribute to our understanding of megacity air pollution and its potential impacts on human health, ecosystem viability, and climate change on urban, regional, and even hemispheric scales. This information will improve significantly the scientific understanding that decision makers in Mexico will need to craft effective policies as well as provide insights to air pollution problems in other megacities around the world.

Acknowledgement

The MILAGRO/INTEX-B participants are grateful for funding from the Mexican Metropolitan Environmental Commission, Mexican Ministry of the Environment, CONACyT, PEMEX, NSF Atmospheric Chemistry Program, DOE Atmospheric Science Program and NASA Tropospheric Chemistry and Radiation Science Programs.

References

[1] UNPD (UN Population Division), World Urbanization Prospect: The 2005 Revision, 2006.

[2] M.J. Molina and L.T. Molina, J. Air & Waste Manage. Assoc. **54**, No. 6, (2004) 644.

[3] L.T. Molina, M.J. Molina, R. Slott, C.E. Kolb, P.K. Gbor, F. Meng, R. Singh, O. Galvez, J.J. Sloan, W. Anderson, X.Y. Tang, M. Shao, T. Zhu, Y.H. Zhang, M. Hu, B.R. Gurjar, P. Artaxo, P. Oyola, E. Gramsch, P. Hidalgo, and A. Gertler, J. Air & Waste Manage. Assoc, 2004. (http://www.awma.org)

[4] L.T. Molina and M.J. Molina, Air Quality in the Mexico Megacity: An Integrated Assessment, Kluwer Academic Publishers: Dordrecht, The Netherlands (2002) pp. 384.

[5] CAM: Programa para Mejorar la Calidad del Aire en el Valle de México 2002-2010, Comisión Ambiental Metropolitana, Mexico, 2002.

[6] L.T. Molina, M.J. Molina, R. Favela, A. Fernandez-Bremauntz, R. Slott and M. Zavala. Cleaning the Air: A Comparative Study in Air Quality in the Mexico Megacity: An Integrated Assessment, Molina, L.T., Molina, M.J., Eds., Kluwer Academic Publishers (2002) 21-59.

[7] J. Evans, J. Levy, J. Hammitt, C. Santos-Burgoa, M. Castillejos, M. Caballero-Ramirez, M. Hernandez-Avila, H. Riojas-Rodriguez, L. Rojas-Bracho, P. Serrano-Trespalacios, J.D. Spengler, and H. Suh, Health benefits of air pollution control, in Air

Quality in the Mexico Megacity: An Integrated Assessment, Molina, L.T., Molina, M.J., Eds., Kluwer Academic Publishers, 103-136, 2002.

[8] L.T. Molina, C.E. Kolb, B. de Foy, B.K. Lamb, W.H. Brune, J.L. Jimenez, R. Ramos-Villegas, J. Sarmiento, V.H. Paramo-Figueroa, B. Cardenas, V. Gutierrez-Avedoy, and M.J. Molina, Atmos. Chem. Phys. **7**, (2007) 2447.

[9] J.D. Fast et al., Atmos. Chem. Phys. **7**, (2007) 2233.

[10] B. de Foy, J. Fast, S.J. Paech, D. Phillips, J.T. Walters, R.L. Coulter, T.J. Martin, M.S. Pekour, W.J. Shaw, P.P. Kastendeuch, N.A. Marley, A. Retama and L.T. Molina, Atmos. Chem. Phys., **8**, (2008) 1209.

[11] B. de Foy, E. Caetano, V. Magaña, A. Zitácuaro, B. Cárdenas, A. Retama, R. Ramos, L.T. Molina and M.J. Molina, Atmos. Chem. Phys. **5** (2005) 2267.

[12] W.J. Shaw, M.S. Pekour, R.L. Coulter, T.J. Martin, and J.T. Walters, Atmos. Chem. Phys. Discuss. **7** (2007) 15025.

[13] S.P. Burton, R.A. Ferrare, C.A. Hostetler, J.W. Hair, A. Cook, D. Harper, M.D. Obland, and R.R. Rogers, Planetary boundary layer (PBL) heights derived from NASA Langley airborne high spectral resolution lidar (HSRL) data acquired during TexAQS/GoMACCS, CHAPS, and MILAGRO, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A51B-0342 (2007).

[14] B. de Foy, J.R. Varela, L.T. Molina and M.J. Molina, Atmos. Chem. Phys. **6**, (2006) 2321.

[15] P. Voss, et al., Reconstruction of trajectories, mixing and Dispersion of a Mexico City pollution outflow event using in-situ observations from free-floating altitude-controlled balloons, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A41F-07 (2007).

[16] CAM: Inventario de emisiones de la atmósfera. Zona Metropolitana del Valle de México 2004, Comisión Ambiental Metropolitana, Mexico (2006).

[17] E. Velasco, B. Lamb, S. Pressley, E. Allwine, H. Westberg, T. Jobson, M. Alexander, P. Prazeller, L. Molina, and M. Molina, Geophys. Res. Lett., 32, L20802, doi:10.1029/ 005GL023356, 2005.

[18] E. Velasco, et al., Atmos. Chem. Phys. **7**, (2007a) 329.

[19] E. Velasco, R. Grivicke, S. Pressley, G. Allwine, T. Jobson, H. Westberg, B. Lamb, and L. Molina, Eddy covariance flux measurements of pollutant gases in the Mexico City urban area: A useful technique to evaluate emissions inventories, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A13I-02 (2007b).

[20] R. Grivicke, S. Pressley, J. Jimenez, L. Alexander, E. Nemitz, E. Velasco, T. Jobson, H. Westberg, R. Ramos, L.T. Molina, B. Lamb, Eddy Covariance Flux Measurements of Urban Aerosols During the MILAGRO Mexico City Field Campaign, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A23C- 1471 (2007).

[21] M. Zavala, S. C. Herndon, R. S. Slott, E. J. Dunlea, L. C. Marr, J. H. Shorter, M. Zahniser, W. B. Knighton, T. M. Rogers, C. E. Kolb, L. T. Molina and M. J. Molina Atmos. Chem. Phys. **6** (2006) 5129.

[22] M. Zavala, S. Herndon, E. Wood, T. Onasch, B. Knighton, M.J. Molina, C.E. Kolb, L.T. Molina, What does the future hold for Mexico City? Trends in Emissions from Combustion Sources, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A23C-1478 (2007).

[23] Yokelson, R. J. Yokelson, R., Urbanski, S., Atlas, E., Toohey, D., Alvarado, E., Crounse, J., Wennberg, P., Fisher, M., Wold, C., Campos, T., Adachi, K., Buseck, P. R., Hao W. M., Atmos. Chem. Phys. **7** (2007) 5569.

[24] R.c. Moffet, B. de Foy, L.T. Molina, M.J. Molina and A. Prather, Atmos. Chem. Phys. Discuss. **7** (2007) 6413.

[25] E.A. Stone, D.C. Snyder, R.J. Sheesley, A.P. Sullivan, R.J. Weber, and J.J. Schauer, Atmos. Chem. Phys. **8** (2008) 1249.

[26] Querol, X., Pey, J., Minguillon, M. C., Perez, N., Alastuey, A., Viana, M., Moreno, T., Bernabe, R. M., Blanco, S., Cardenas, B., Vega, E., Sosa, G., Escalona, S., Ruiz, H., Artiñano, B., PM Atmos. Chem. Phys. **8** (2008) 111.

[27] Case Hanks, A.T, L. Huey, D. Tanner, O. Vargas, S. Sjostedt, J. R. Olson, G. Chen, B. Lefer and D. R. Blake, Photochemical activity in Mexico City during MILAGRO 2006: results from the T1 site, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A33D-1541 (2007).

[28] S. Dusanter, D. Vimal, P.S. Stevens, R. Volkamer and L.T. Molina, Hydroxyl and

hydroperoxy radical chemistry during the MCMA-2006 field campaign: Measurement and model comparison, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A22C-06, (2007).

[29] C.A. Cantrell and R.S. Anderson, Behavior of tropospheric peroxy radicals during several recent airborne measurement campaigns, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A11C-0596 (2007).

[30] J. Zheng, R. Zhang, E.C. Fortner, L.T. Molina, A.C. Aiken, J.T. Jimenez, K. Gäggeler, J., Dommen, S. Dusanter, P.S. Stevens and X. Tie, Atmos. Chem. Phys. Discuss. **8** (2008) 4877.

[31] T.R. Shirley, W.H. Brune, X. Ren, J. Mao, R. Lesher, B. Cardenas, R. Volkamer, L.T. Molina, M.J. Molina, B. Lamb, E. Velasco, T. Jobson and M. Alexander, Atmos. Chem. Phys., **6** (2006) 2753.

[32] L. Nummermacker, J. Weinstein-Lloyd, L. Kleinman, S. Springston, P. Daum, B. Hillery, and B. Giebel, Atmos. Chem. Phys. (2008) unpublished.

[33] W. Lei, B. de Foy, M. Zavala, R. Volkamer, and L.T. Molina, Atmos. Chem. Phys. **7**, (2007) 1347.

[34] X. Tie, S. Madronich, G. Li, Z. Ying, R. Zhang, A. Garcia, J. Lee- Taylor and Y. Liu, Atmos. Environ. **41** (2007) 1989.

[35] W. Lei, B. de Foy, M. Zavala, R. Volkamer, and L.T. Molina, Characterizing ozone production and response and their evolution under different meteorological conditions in Mexico City. Atmos. Chem. Phys. (2008) unpublished

[36] R. Volkamer, P.M. Sheehy, L.T. Molina, and M.J. Molina, Atmos. Chem. Phys. Discuss., **7** (2007) 5365.

[37] P. Sheehy, M., R. Volkamer, L. T. Molina, and M. Molina, Atmos. Chem. Phys. Discuss., Atmos. Chem. Phys. (2008) unpublished.

[38] E.C. Apel et al., Observations of volatile organic compounds downwind of Mexico City during MIRAGE- MEX, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A41F-02, (2007).

[39] F. Flocke et al., Reactive nitrogen chemistry in Mexico City outflow: a unique case, Eos Trans. AGU, 88(52), Fall Meet. Suppl. Abstract A31E-05 (2007).

[40] R.A. Zaveri, E. G. Chapman, R. C. Easter, J. D. Fast, F. Flocke, L. I. Kleinman, S. Madronich, S. R. Springston, P. B. Voss and A. Weinheimer, Modeling gas-aerosol processes during MILAGRO 2006, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A33D-1570 (2007).

[41] A. Hodzic et al, Contribution of dust particles to the heterogeneous removal of acidic gases from the atmosphere during the MIRAGE experiment, Eos Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A23C-1476 (2007).

[42] Jr. Arellano, A., K. Raeder, J. Anderson, P. Hess, L. Emmons, D. Edwards, G. Pfister, T. Campos and G. Sachse, Atmos. Chem. Phys. Discuss. (2008).

[43] D. Salcedo, et al., Atmos. Chem. Phys. **6** (2006) 925.

[44] R. Volkamer, J.L. Jimenez, F. San Martini, K. Dzepina, Q. Zhang, D. Salcedo, L.T. Molina, D.R. Worsnop and M.J. Molina, Geophys. Res. Lett., **33**, L17811, doi:10.1029/2006 GL026899 (2006).

[45] S. Herndon, T.B. Onasch, E.C. Wood, J. H. Kroll, M.R. Canagaratna, J.T. Jayne, M.A. Zavala, W.B. Knighton, C. Mazzoleni, M.K. Dubey, I.M. Ulbrich, J.L. Jimenez, R. Seila, J.A. de Gouw, B. de Foy, J. Fast, L.T. Molina, C.E. Kolb and D.R. Worsnop, Geophys. Res. Lett., (2007) unpublished.

[46] A.C. Aiken et al., Environ Sci., Technol. (2008) in press.

[47] L.I. Kleinman, et al., Atmos. Chem. Phys., **8**, (2008) 1559.

[48] P.F. DeCarlo et al., Atmos. Chem. Phys. Discuss. **7** (2007) 18269.

[49] IMP (2006) Estudio de las emisiones de la zona industrial de Tula y su impacto en la calidad del aire regional. Instituto Mexicano del Petróleo PS-MA-IF-F21393-1, Noviembre